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(21) International Application Number: PCT/EP00/00034 (22) International Filing Date: 5 January 2000 (05.01.00) (30) Priority Data: 60/117,417 27 January 1999 (27.01.99) US (71) Applicant (for all designated States except US): HUNTSMAN ICI CHEMICALS, LLC [US/US]; 500 Huntsman Way, Salt Lake City, UT 84108 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BURNS, Steve, B. [US/US]; 1107 Belmont Avenue, Westmont, NJ 08108 (US). PHANOPOULOS, Christopher [GB/BE]; Lindenberg 23, B-3080 Tervuren-Vossem (BE). VAN DEN BOSCH, Christel [BE/BE]; Mechelbaan 19, B-3200 Aarschot (BE). COLEMAN, Paul, D, Jr. [US/US]; 508 Quail Court, Sewell, NJ 08080 (US). (74) Agent: MOENS, Mamix, Karel, Christiane; Huntsman ICI Europe Ltd., Huntsman Polyurethanes, Intellectual Property Dept., Everslaan 45, B-3078 Everberg (BE).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: MOISTURE-ACTIVATED ADHESIVE COMPOSITIONS (57) Abstract A moisture-activated adhesive composition comprising the reaction product of: (A) a polyisocyanate selected from (a) a blend of polymeric MDI and pure MDI and/or from (b) an isocyanate-terminated prepolymer; (B) an isocyanate-reactive component comprising at least one aliphatic tertiary amine group-containing polyol made by alkoxylation of amines or aminoalcohols, characterized in that the total ethylene oxide content by weight of the total adhesive composition is more than 2.5 %.		

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MOISTURE - ACTIVATED ADHESIVE COMPOSITIONSFIELD OF THE INVENTION

The present invention is directed to rapid curing moisture-activated adhesive compositions and methods for their production and a process for bonding multiple substrates using said composition. More specifically, the present invention is directed to specific moisture-activated adhesive compositions which are cold curable in the presence of high moisture content cellulosic or lignocellulosic substrates.

BACKGROUND OF THE INVENTION

In recent years, the use of "engineered lumber" products by the construction industry has become increasingly common - primarily because the availability and cost of adequate quality sawn lumber have become increasingly unfavorable. However, the performance of "engineered lumber" products, which are formed by adhering smaller pieces of wood together into a composite material, represents some major challenges to the adhesives formulator.

Engineered lumber products on the market today, such as finger-jointed lumber, wood I-beams, and glue-laminated beams (glu-lams), utilize a variety of adhesive systems, including phenol - formaldehyde (PF) based adhesives, polyvinylacetate (PVA) adhesives, and isocyanate - based emulsion adhesives. Unfortunately, each of these adhesive systems has limitations, which compromises the effectiveness of the resultant engineered lumber composite.

PF based adhesives require a great deal of heat and time in order to cure, and are sensitive to high levels of moisture in the wood. Use of these adhesives systems requires engineering controls to maintain a low moisture content, and to ensure adequate bonding occurs within the composite. The necessity for such costly catalyst and engineering controls increases production costs, and limits productivity, which in turn limits the competitiveness of engineered lumber in the marketplace. Another major problem associated with these adhesives is their "green strength". These adhesives do not produce adequate bond strength immediately - they typically need to "cure" in order to reach their full potential. This cure time is a matter of hours, often days - which further adds to production costs

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PVA adhesives have limited strength. To date, they have not proven to be suitable for use in structural applications, which require physical properties of a certain minimum standard. For example, no commercially available PVA bonded engineered lumber product can meet the ASTM D2259 standard, a frequent requirement for structural lumber applications. Like the PF adhesives discussed above - these systems also suffer from the limitations of slow green strength development, and a dependency on a great deal of heat and time to ensure adequate bond strengths.

Isocyanate-crosslinked latex emulsion adhesives, also have limitations in that these systems also suffer from the limitations of slow green strength development, and a dependency on a great deal of heat to ensure adequate bonding.

Polyisocyanate based adhesive compositions have also been identified for composite wood applications. Examples are moisture curable urethane-modified polyisocyanate adhesives described in EP-B-723 561 which discloses urethane-modified polyisocyanate adhesives for use in plywood panel wood composites. These compositions contain auto catalytic species, designed to increase the reactivity of the polyisocyanate, enabling cure at ambient temperatures in a matter of minutes. However, for engineered lumber products, the different processing requirements between panels and lumber becomes extremely important. As a consequence none of the existing polyisocyanate products, designed for relatively thin composite wood panels, exhibits sufficient reactivity to truly be cost-effective in relatively thick engineered lumber applications.

It is therefore an object of the present invention to provide an adhesive composition especially designed for engineered lumber which impart adequate strength and reactivity and tack without the need for costly catalyst and processing/engineering controls to overcome inherent problems, such as: maintaining low raw material moisture contents, providing a great deal of heat and time in order to cure the adhesive, and protracted "green" strength development.

These objectives are met by the present adhesive compositions, which demonstrate excellent adhesive properties with a prolonged pot life, accelerated cure, particularly at room temperature. Surprisingly, the compositions according to the present invention provide equal performance than those compositions as described in EP 0 723 561. The present compositions are activated by the moisture present in the substrate with which they are being used and thus, they may be most effectively used with substrates having a relatively high moisture content, even as high as 20% or more. Accordingly, the present compositions are effectively used with various types of lignocellulosic materials and are particularly useful in the preparation of engineered lumber products as discussed above.

SUMMARY OF THE INVENTION

The present invention relates to a moisture-activated adhesive composition comprising the reaction product of (A) polyisocyanate selected from either (a) a blend of polymeric MDI and pure MDI and/or from (b) an isocyanate-terminated prepolymer. (B) an isocyanate-reactive component comprising at least one aliphatic tertiary amine group-containing polyol made by alkoxylation of amines or aminoalcohols characterized in that the total ethylene oxide content by weight of the total adhesive composition is more than 2.5%

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, the polyisocyanate component is selected from either (a) a blend of polymeric MDI and pure MDI and/or (b) an isocyanate-terminated prepolymer. In accordance with the present invention, the blend of polymeric MDI and pure MDI have been found to provide improved penetration into the lignocellulosic substrate and higher wood failure as opposed to glueline failure. A commercially available pure MDI product suitable for use in the present invention is Rubinate™ 44 available from ICI Americas Inc. The preferred blends contain polymeric MDI to pure MDI in ratios of 95:5 to 50:50 and preferably 60:40 to 80:20.

The isocyanate-terminated prepolymers as used herein, the term "isocyanate-terminated prepolymer" includes the prepolymer as well as the pseudoprepolymer, i.e., a mixture of the prepolymer and the polyisocyanate from which the prepolymer is prepared. The isocyanate-

terminated prepolymer useful in the present compositions should have a free isocyanate (NCO) content of from 10 to 29%, preferably 16 to 29%. In general, the polymeric polyisocyanate may be prepared by the reaction of an excess of a polyisocyanate and a polyol, including aminated polyols or imino/enamines thereof.

5

Suitable polyols for preparing the isocyanate-terminated prepolymers include:

(a) polyether polyols, thioether polyols and/or hydrocarbon-based polyols having a molecular weight of from 1000 to 6000 and an average hydroxyl functionality of from 1.8 to 4

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(b) polyester polyols having a molecular weight of 1000 or more and an average hydroxyl functionality of from 1.9 to 4.

15 Particularly preferred isocyanate-terminated prepolymers useful in the present invention are MDI prepolymers, which are the reaction product of an excess of polymeric MDI and polyether polyols. The polyether polyols are preferably diols or triols having hydroxyl values of 25 to 120. The polyol should have a number average molecular weight in the range of 1000 to 6000. Such prepolymers should generally have a free-NCO content of more than 10%,
20 preferably more than 16% and most preferably 16 to 29%. Suitable polymers are those in which the stoichiometric ratio of isocyanate (NCO) to hydroxyl (OH) exceeds 1:1. Rubinate™ M available from ICI Americas is a suitable polymeric MDI composition useful in the present invention.

25 The second component of the present compositions is an isocyanate-reactive component characterized in that the total ethylene oxide content by weight of the total adhesive composition is more than 2.5%. More preferably, at least 40% of the total ethylene oxide content is present as part of the reactant.

30 Reactants suitable for the present invention are reactants comprising at least one aliphatic tertiary amine group-containing polyol having an ethylene oxide content of at least 1%.

Preferably, the ethylene oxide content of the reactant is from 1 to 90%, preferably 5 to 60. The aliphatic tertiary amine group-containing polyol provides an ethylene oxide content in the prepolymer of 0.01 to 27%, preferably 0.35 to 12%. Most preferred, the weight ratio of ethylene oxide to propylene oxide in the total composition is at least 1 to 5, said propylene oxide or ethylene oxide being part of the reactant and/or from an additional polyol being present in the total composition.

The aliphatic tertiary amine group-containing polyols are the known alkoxylation products of amines or aminoalcohols with at least two active hydrogen atoms with ethylene oxide and optionally propylene oxide. Suitable initiator molecules include: ammonia, ethylene diamine, hexamethylene diamine, methylamine, diaminodiphenyl methane, aniline, ethanolamine, diethanolamine, N-methyl diethanolamine, and tetrahydroxyl ethyl ethylenediamine.

Suitable aliphatic tertiary amine group-containing polyols are those wherein the initiator comprises 1 to 18 and preferably 1 to 6 carbon atoms. Suitable aliphatic tertiary amine group-containing polyols have an average molecular weight of about 1500 to 10,000 and preferably 1500 to 6000 and an average OH functionality of 1.8 to 6.0.

Preferred amine group-containing polyols for use in the present invention includes those prepared from ethylene diamine, triethylene tetramine and triethanolamine.

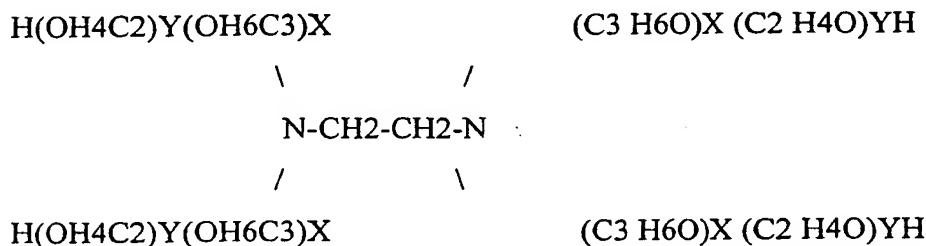
The present compositions comprise the reactant such as the aliphatic tertiary amine group-containing polyol component, in an amount of 1 to 50%, preferably 7 to 30% and most preferably 10 to 20% by weight based upon the total amount of isocyanate and polyol in the composition.

In its most preferred form, the amine group-containing polyol is an ethylene diamine-based polyol containing ethylene oxide. Suitable ethylene diamine-based polyols are those having an ethylene oxide content of 1 to 90%, preferably 5 to 60%. The ethylene oxide content refers to the amount of ethylene oxide utilized in the preparation of the polyols as discussed above.

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During production, the ethylene oxide reacts with the initiator. The polyols should have a molecular weight in the range of 1500 to 6000.

Suitable ethylene diamine-based polyols useful in the present compositions include those of the following formula:



wherein x is an integer of 1.0 to 29.0, preferably 4.0 to 20 and most preferably 4.0 to 14 and y is an integer of 0.1 to 10.0 and preferably 2.0 to 4.0. Suitable ethylene diamine-based polyols are available commercially, such as the "Synperonic T" series of polyols available from ICI Americas Inc.

Preferably, the total ethylene oxide content by weight of the total adhesive composition is more than 2.5%. Most preferred, at least 40% of the total ethylene oxide content is present as part of the reactant. Polypropylene oxide based reactants or additional polypropylene oxide based polyols may be used for the present compositions, preferably whereby the weight ratio of ethylene oxide to propylene oxide is at least 1 to 8, said propylene oxide being part of the reactant and/or from an additional polyol being present in the total composition.

Preferably, the concentration of nitrogen in the amine group-containing polyol is 0.002 to 0.05 eqN/100g.

The said adhesive composition may be produced in any number of ways such as, but not limited to:

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- (i) Sequentially mixing the components at temperatures 25-80oC (with the proviso that when using pure MDI it is used above 42oC). Said mixtures are then allowed to react.
- (ii) Sequentially mixing and pre-reacting components (a) and (b).
- 5 (iii) Pre-reacting part of the isocyanate component with one of the isocyanate-reactive components, then separately pre-reacting the rest of the isocyanate component with the other isocyanate-reactive component, and blending the two prepolymers together.

10 Catalysts can additionally be incorporated into the present compositions to further enhance the cure rate of the compositions. Examples of appropriate catalysts are, e.g., tertiary amine catalysts. Suitable tertiary amine catalysts are available commercially, as Niox A-4, from Union Carbide and Thancat DMDEE, from Texaco. Most preferably, the Niox A-4 catalyst is used in the relatively slower cure systems.

15 It has been found however, that reactivity can be controlled by the ethylene oxide in total composition , so limiting the number of formulations which require the addition of extra catalysts.

20 Other additives such as fungicides, tackifiers, UV stabilizers, viscosity reducers, plasticisers, fillers and extenders as well as surface tension modifying agents can be added depending on the specific application or manufacturing procedure. Furthermore, other adhesives such as, but not limited to, UF, PF and PRF can also be incorporated into the formulation.

25 The adhesive compositions of the present invention have been found to have a pot life of approximately three months or more under moisture-free conditions when mixed prior to application to a substrate.

30 The present compositions are also "cold curable", i.e., may be cured at a temperature of 10oC to room temperature although they can also be hot cured. Thus, the present compositions may be cured at temperatures of from 10oC to 250oC. Preferably the present compositions are

cured at a temperature of 23oC to 125oC. Generally, most systems will cure at room temperature in 10-30 minutes.

The adhesive compositions of the present invention may be used to bond many different types of moisture-containing substrates. It is preferred that at least one of the substrates be selected from the group consisting of wood, paper, rice hulls, cement, stone, cloth, grass, corn husks, bagasse, nut shells, polymeric foam films and sheets, polymeric foams and fibrous materials. Preferably, the present composition is used to fabricate multi-substrate composites or laminates. Those composites or laminates of particular interest being those comprising lignocellulosic or cellulosic materials, such as wood or paper, to prepare products such as finger joints, "Glulam" and I- Beams, plywood, wafer board, particleboard, fiberboard, chipboard, and oriented wood products, such as "Parallam", available from McMillan Bloedell.

As the present adhesive compositions are moisture-activated, it is important that the substrates have relatively high moisture contents. Specifically, the substrates should have moisture contents of at least 7%. Preferably, the substrates have moisture contents of 10 to 20% by weight and more preferably 12 to 15% by weight

When used to bond multiple substrates together, the present composition is applied to a surface of a first substrate. A surface of a second substrate is then contacted with the surface of the first substrate containing the present composition. Pressure is then applied to the contacted surfaces and the adhesive compositions are allowed to cure. The surface of the second substrate against which the first substrate is contacted is generally not coated with the present adhesive composition. However, that surface may also be coated prior to contacting the substrates.

The present invention is further directed to a process for bonding multiple substrates comprising

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- (1) applying to a surface of a first substrate the present moisture-activated adhesive composition as defined above and contacting the surface of the first substrate with a surface of a second substrate
- (2) applying pressure to the contacted surfaces, and
- 5 (3) curing the adhesive composition.

Additionally, independent of the moisture content, additional water can be applied to in the following manner

- 10 (a) the first substrate surface prior to the application of the present composition,
- (b) on top of the resin, after application to the first substrate surface and/or
- (c) to the second substrate surface prior to contacting the first, resinated substrate surface, or any combinations thereof, to speed up the reaction

15 Such additions of moisture are called "misting". Misting can optionally be used to increase the accessibility of water to the reactive isocyanate. Preferably, the application levels of water should not exceed 5% of the resin loading.

20 The present adhesive compositions also provide cold tack immediately after application to a substrate. This is particularly useful for pre-press operations where mechanical handling is often necessary. Cold tack is achieved naturally by the present composition adhesives, described in this invention. The present compositions may be used as additives to other resins and adhesives, which require improved tack properties.

25 The present adhesive compositions may be applied to the surfaces of the substrates in any conventional manner. For example, the surface may be coated with the composition by spraying, brushing, etc. Suitable means for applying the adhesive compositions to the surface of the substrate for a particular application will be evident to one skilled in the art from the present disclosure.

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After the coated substrates are contacted with each other, pressure is applied thereto. The pressure should be sufficient to cause the surfaces to adhere to one another. Generally, the amount of pressure and the time period for which the pressure is applied are not limited and specific pressures and times will be evident to one skilled in the art from the present disclosure. However, it has been found preferable that a pressure of approximately 10 to 200 psi (equivalent to 69 to 1380 kPa) be applied for 10 to 20 minutes to cause appropriate adhesion for most substrates. Further processing can generally be conducted on the treated substrates in less than one hour.

- 10 The invention is now illustrated by the following examples, which are not intended to limit the scope of the invention.

EXAMPLES

- 15 The following adhesive compositions were prepared in accordance with the present invention.

Example 1

	MDI prepolymer	80
20	Polyol 1	20

The MDI prepolymer had an NCO content of 24.9% and was prepared by reacting Rubinol F-456 (a polyether diol available from ICI Americas Inc.) with a 69/31 blend of polymeric MDI to pure MDI. The polymeric MDI used was Rubinate™ M and the pure MDI used was Rubinate™ 44, both available from ICI America Inc. Polyol 1 was "Synperonic T 304" which is an ethylene diamine-based polyol available from ICI Americas Inc.

25 Total EO % by weight of the total adhesive composition is 8%.

Comparison example 2a

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	MDI prepolymer	80
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Polyol 2

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The MDI prepolymer had an NCO content of 24.9% and was prepared by reacting Rubinol F-456 (a polyether diol available from ICI Americas Inc.) with a 69/31 blend of polymeric MDI to pure MDI. The polymeric MDI used was Rubinate™ M and the pure MDI used was Rubinate™ 44, both available from ICI Americas Inc. Polyol 2 was "Synperonic T 701" which is an ethylene diamine-based polyol available from ICI Americas Inc. Total EO % by weight of the total adhesive composition is 2.2%.

10 Example 2b

	MDI prepolymer	63.58
	Polyol 2	1.91
	Polyol 1	8.27
15	Niax A-4	0.64
	Calcium Carbonate No.7	25.43
	SAG 47	0.07

Same as example 2a with SAG 47 is an antifoam agent available from Union Carbide. NiaxA-4 is a suitable tertiary amine catalysts available from Union Carbide. Total EO % by weight of the total adhesive composition is 1.6%.

Example 3

25	MDI prepolymer	84.4
	Polyol 1	15.05
	DMDEE	0.05

The MDI prepolymer had an NCO content of 25.2% and was prepared by reacting Rubinol F-456 (a polyether diol available from ICI Americas Inc.) with a 71.2/28.8blend of polymeric MDI to pure MDI. The polymeric MDI used was Rubinate™ M and the pure MDI used was

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Rubinate™ 44, both available from ICI Americas Inc. Polyol 1 was "Synperonic T 304" which is an ethylene diamine - based polyol available from ICI Americas Inc.

Total EO % by weight of the total adhesive composition is 6%.

5 Example 4

MDI prepolymer	80
Polyol 1	20

10 The MDI prepolymer had an NCO content of 24.9% and was prepared by reacting Rubinol F-481 (a polyether diol available from ICI Americas Inc.) with a 69/31 blend of polymeric MDI to pure MDI. The polymeric MDI used was Rubinate™ M and the pure MDI used was Rubinate™ 44, both available from ICI Americas Inc. Polyol 1 was "Synperonic T 304" which is an ethylene diamine - based polyol available from ICI Americas Inc.

15 Total EO % by weight of the total adhesive composition is 12%.

Example 5

	Polymeric MDI	45
20	44 MDI	20
	Rubinol F456	15
	Synperonic T 304	20

25 The products were made by sequential addition of the different components. The final NCO, viscosity and properties are the same as in Example 1.

Total EO % by weight of the total adhesive composition is 8%.

Results :

30 Reactivity test measured as the time taken to start foaming when formulation is contacted on a 10% moisture containing aspen wood showed that the formulation

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according to example 1 and 4 is significantly faster than formulation of example 2 and equivalent to the formulation of example 3 (formulation with catalyst).

Formulations given in examples 1 and 4, were used to construct single lap joints using 150 x 25 x 3 mm tangentially cut aspen wood. Overlaps were 25 x 25 mm and resin loadings were 12 mg.m⁻². The lap joints were cured at room temperature for 15 minutes and tested to failure. Two sets of samples were produced. In the first instance, the resin was applied to the wood of moisture content 10%. In the second case, after the application of the adhesive, an additional 5% (based on adhesive weight), water content was applied by spray onto the adhesive layer. The loads to failure were recorded. The results, listed below, show a much higher tensile shear strength and higher percentages of wood failure for the systems with added water.

	Tensile Strength failure loads in MPa	
	Without mist	With mist
Example 1	0.6	3.5
Example 5	0.6	3.5

CLAIMS

1. A moisture-activated adhesive composition comprising the reaction product of

5 (A) a polyisocyanate selected from (a) a blend of polymeric MDI and pure MDI and/or from (b) an isocyanate-terminated prepolymer.

(B) an isocyanate-reactive component comprising at least one aliphatic tertiary amine group-containing polyol made by alkoxylation of amines or aminoalcohols

10 characterized in that the total ethylene oxide content by weight of the total adhesive composition is more than 2.5%

15 2. A moisture-activated adhesive composition according to claim 1 whereby at least 40% of the total ethylene oxide content is present as part of the reactant

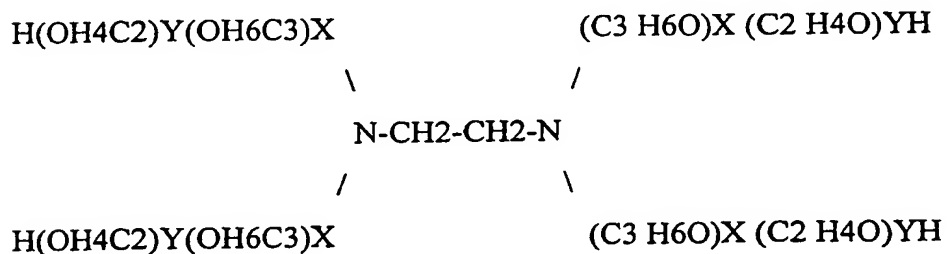
20 3. A moisture-activated adhesive composition according to claims 1-2 whereby the weight ratio of ethylene oxide to propylene oxide is at least 1 to 8, said propylene oxide being part of the reactant and/or from an additional polyol being present in the composition

4. A moisture -activated adhesive composition according to claims 1-3 whereby the total nitrogen concentration of the total composition is from 0.002 to 0.05 eqN/100 g

25 5. A moisture-activated adhesive composition according to claims 1-4, wherein said polymeric polyisocyanate is a polymeric diphenylmethane diisocyanate.

30 6. A moisture-activated adhesive composition according to claim 1-5, wherein said isocyanate-terminated prepolymer having an NCO content of 10 to 29 %.

7. A moisture-activated adhesive composition according to claim 6, wherein said isocyanate-terminated prepolymer is the reaction product of polymeric diphenylmethane diisocyanate and a polyether polyol having a molecular weight of from 1000 to 6000.
8. A moisture-activated adhesive composition according to claim 1, wherein said reactant is an aliphatic tertiary amine group-containing polyol having an ethylene oxide content of 1 to 90 %.
9. A moisture-activated adhesive composition according to claim 8, wherein said aliphatic tertiary amine group-containing polyol has an ethylene oxide content of 5 to 60 %.
10. A moisture-activated adhesive composition according to claim 1, wherein said aliphatic tertiary amine group-containing polyol has a molecular weight of 1500 to 10,000 and comprises an initiator having 1 to 18 carbon atoms.
11. A moisture-activated adhesive composition according to claim 1, wherein said aliphatic tertiary amine group-containing polyol is prepared from a compound selected from the group consisting of ethylene diamine, triethylene tetramine and triethanolamine.
12. A moisture-activated adhesive composition according to claim 11, wherein said aliphatic tertiary amine group-containing polyol is an ethylene diamine-based polyol having the following formula:



wherein x is an integer of 1 to 29.0 and y is an integer of 0.1 to 10.

- 5 13. A moisture-activated adhesive composition according to claim 1, further comprising a catalyst.
14. A process for bonding multiple substrates comprising
- 10 (1) applying to a surface of a first substrate a moisture-activated adhesive composition as defined in any one of the preceding claims
- (2) contacting said surface with a surface of a second substrate
- (3) applying pressure to the contacted surfaces, and
- (4) curing said adhesive composition.
- 15 15. A process according to claim 14, wherein said substrate has a moisture content of at least 7 % by weight.
16. An engineered lumber product prepared by the process according to claim 14.
- 20 17. A process for bonding according to claim 16, wherein additional moisture is applied to the first substrate surface, the surface of the applied adhesive and/or the surface.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/00034

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09J175/12 C08G18/50 C08G18/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09J C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 10555 A (IMPERIAL CHEMICAL INDUSTRIES) 20 April 1995 (1995-04-20) the whole document & EP 0 723 561 A cited in the application ---	1-17
X	US 5 562 148 A (SCHNEIDER) 8 October 1996 (1996-10-08) column 2, line 50 -column 4, line 34 --- -/--	1-5

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 106, no. 18, May 1987 (1987-05) Columbus, Ohio, US; abstract no. 139474h, TANAKA ET AL: "Thixotropic polyurethane adhesives" page 52; column 1; XP002114085 abstract & JP 61 228075 A (MYOJO)</p>	1
A	<p>EP 0 063 534 A (GOODYEAR TIRE AND RUBBER) 27 October 1982 (1982-10-27) page 4, line 16 -page 6, line 30</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/00034

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9510555 A	20-04-1995	AU 702132 B	11-02-1999
		AU 7813794 A	04-05-1995
		CA 2171202 A	20-04-1995
		CN 1133053 A, B	09-10-1996
		DE 69407306 D	22-01-1998
		DE 69407306 T	16-04-1998
		EP 0723561 A	31-07-1996
		ES 2109735 T	16-01-1998
		HK 1005621 A	15-01-1999
		JP 9503806 T	15-04-1997
		NZ 274183 A	24-11-1997
US 5562148 A	08-10-1996	NONE	
JP 61228075 A	11-10-1986	NONE	
EP 63534 A	27-10-1982	US 4552934 A	12-11-1985
		AU 8230182 A	14-10-1982
		JP 57182374 A	10-11-1982
		CA 1212496 A	07-10-1986

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